

WE CLAIM:

1. A process for the hydroformylation of an optionally substituted ethylenically unsaturated compound by reaction thereof with carbon monoxide and hydrogen in the presence of a catalyst system comprising:

- (a) a source of Group VIII metal cations;
- (b) a diphosphine ligand having the general formula (I):



wherein X^1 and X^2 each independently represent an optionally substituted cyclic group with at least 5 ring atoms, of which one is a phosphorus atom, and R represents a bivalent optionally substituted bridging group which is connected to each phosphorus atom by a sp^2 hybridized carbon atom;

- (c) an acid having a $pK_a < 3$, measured in an aqueous solution at 18 °C, or a salt derived therefrom; and
- (d) a source of halide anions.

2. The process of claim 1 wherein R is selected from the group consisting of alkene, cycloalkene, and aromatic groups, wherein the carbon atoms connected to a phosphorus atom are connected via an unsaturated bond to another atom.

3. The process of claim 1 wherein R is a bivalent optionally substituted aromatic bridging group with both phosphorus atoms bound to the same sp^2 hybridized carbon atom.

4. The process of claim 1 wherein R is a bivalent optionally substituted aromatic bridging group having at least 2 sp^2 hybridized carbon atoms and each phosphorus atom is connected to a separate sp^2 hybridized carbon atom.

5. The process of claim 1 wherein the bridge in R contains 2 to 6 carbon atoms.
6. The process of claim 5 wherein the bridge in R contains 2 to 4 carbon atoms.
7. The process of claim 6 wherein the bridge in R contains at least 2 sp^2 hybridized carbon atoms.
8. The process of claim 1 wherein X^1 and/or X^2 represent an optionally substituted phospho-bicycloalkyl group with at least 6 ring atoms.
9. The process of claim 1 wherein X^1 and X^2 have 6 to 12 ring atoms.
10. The process of claim 1 wherein the diphosphine ligand (b) is selected from the group consisting of
1,2-P,P'bis(9-phosphabicyclononyl) benzene;
1,2-P,P'bis(9-phosphabicyclononyl) 4-methyl benzene;
3,4-P,P'bis(9-phosphabicyclononyl) thiophene;
1,2-P,P'bis(9-phosphabicyclononyl) cyclopentene; and
1,2-P,P'bis(9-phosphabicyclononyl) cyclohexene.
11. The process of claim 10 wherein the diphosphine ligand (b) is selected from the group consisting of
3,4-P,P'bis(9-phosphabicyclononyl) thiophene; and
1,2-P,P'bis(9-phosphabicyclononyl) cyclopentene.
12. The process of claim 1 wherein the Group VIII metal is selected from the group consisting of rhodium, nickel, palladium, and platinum.
13. The process of claim 12 wherein the Group VIII metal is selected from the group consisting of palladium, and platinum.
14. The process of claim 13 wherein the Group VIII metal is palladium.
15. The process of claim 1 wherein the source of Group VIII metal cations is selected from the group consisting of Pd (II) acetate and Pt (II) acetylacetonate.

16. The process of claim 1 wherein the ethylenically unsaturated compound has 2 to 40 carbon atoms per molecule.
17. The process of claim 16 wherein the ethylenically unsaturated compound is an alkene comprising at least 4 carbon atoms.
18. The process of claim 17 wherein the ethylenically unsaturated compound is an alkene comprising at least 8 carbon atoms.
19. The process of claim 18 wherein the ethylenically unsaturated compound is an alkene comprising 8 to 25 carbon atoms.
20. The process of claim 19 wherein the alkenes are octenes in a mixture of octenes, octadienes, methylheptadienes, and/or dimethyl hexadienes.
21. A diphosphine ligand having the general formula (II):



- wherein X^1 and X^2 each independently represent an optionally substituted cyclic group with at least 5 ring atoms, of which one is a phosphorus atom, and R^2 represents a bivalent optionally substituted bridging group which is connected to each phosphorus atom by a sp^2 hybridized carbon atom, with the proviso that the diphosphine ligand is not 1,2-P,P'bis(9-phosphabicyclononyl) benzene.
22. A diphosphine ligand having the general formula (III):



- wherein X^1 and X^2 each independently represent an optionally substituted cyclic group with at least 5 ring atoms, of which one is a phosphorus atom, and R^3

represents a bivalent cycloalkene group which is connected to each phosphorus atom by a sp^2 hybridized carbon atom.

23. A diphosphine ligand having the general formula (IV):



wherein x^1 and x^2 each independently represent an optionally substituted cyclic group with at least 5 ring atoms, of which one is a phosphorus atom, and R^4 represents a bivalent aromatic group, wherein the aromatic ring contains one or more hetero atoms as a ring atom, which aromatic group is connected to each phosphorus atom by a sp^2 hybridized carbon atom.

24. A catalyst comprising:

- (a) a source of Group VIII metal cations; and
- (b) the diphosphine ligand of claim 23.

25. A catalyst comprising:

- (a) a source of Group VIII metal cations; and
- (b) the diphosphine ligand of claim 21.

26. A catalyst comprising:

- (a) a source of Group VIII metal cations; and
- (b) the diphosphine ligand of claim 22.